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(54) Title: **ELECTRICALLY CONDUCTIVE INK**

(57) Abstract: The invention relates to the use of electrically conductive inks, said inks comprising electrically conductive powder and electrically conducting fibres, wherein the aspect ratio of the fibres is greater than 2:1. The inks are used to form electrically conductive layers, especially in optoelectronic devices such as solar cells. The layers have considerably reduced electrical resistance than if the electrically conductive powder were used alone.



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ELECTRICALLY CONDUCTIVE INK

The present invention relates to the use of conductive inks to form electrically conductive layers, especially in optoelectronic devices.

In any form of electrical power generation device, power conversion losses due to ohmic resistance of internal conductive pathways is usually undesirable and must be kept to a minimum. In conventional solid-state solar cells that convert light energy into electrical energy, such as those based on silicon, printed tracks made e.g. from silver pastes are commonly used to carry the electrical current from the active part of the cell to the external environment. Silver or similar metals are used due to their low electrical resistance. Newer types of solar cells incorporating e.g. solid polymer electrolytes and/or dye-sensitised semi-conductor powders may or may not be able to use conducting tracks based on metal pastes depending upon the chemical environment within the cells and also upon cost considerations. There is therefore a need to develop alternative conducting track and/or electrode materials for use in these types of cells that are more chemically resistant and/or are cheaper.

Particulate materials, such as e.g. carbon, are well-established electrical conductors that have been used as track and electrode material in solar cells. WO 94/15344 discloses a *conductive ink comprising carbon particulate materials*. Particulate carbon has also been used as part of the counter-electrode in dye-sensitised solar cells (so called Graetzel cells), often applied to substrates in the form of a paste or as an ink. However, electrical conductivity in the carbon layer or film produced under these circumstances relies on point-to-point contact between small, frequently micro-sized, carbon particles. Thus the electrical pathway is both tortuous and very sensitive to the physical and chemical nature of the carbon particle surfaces.

It has now been found that if such particulate conductive materials, such as e.g. carbon, are partially replaced by conductive fibres in inks, the resultant conductive inks or layers produced therefrom are significantly more conductive than an equivalent volume of particulate materials.

Thus, in the first aspect the present invention provides for the use of an electrically conductive ink comprising an electrically conductive powder and electrically conductive fibres wherein the aspect ratio of the fibres is greater than 2:1, to form an electrically conductive layer.

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The electrically conductive powder suitably comprises one or more conductive particulate materials such as carbon, nickel, tungsten and F-doped tin oxide, but is preferably carbon powder. Specific examples of carbon powder that can be used include, but are not limited to, Vulcan XC72R (Cabot Carbon Limited, Stanlow, Ellesmere Port, South Wirral, L65 4HT, UK) and TIMREX KS15 Graphite (Timcal Ltd, CH-6743, Bodio, Switzerland). The electrically conductive powder suitably has a surface area in the range from 5 to 1000m²/g, preferably from 20 to 250m²/g.

The electrically conductive fibres have an aspect ratio of greater than 2:1, preferably greater than 10:1. The fibres may be any electrically conductive fibres, including carbon, nickel, tungsten and F-doped tin oxide, but are preferably carbon fibres. The fibres must be chosen to ensure that they are chemically compatible with the other components. The fibres are suitably of a length of at least 1 micron, preferably greater than 1mm. The conducting fibres preferably have a thickness of not more than 100 microns, preferably not more than 50 microns. Specific examples of conductive carbon fibres that may be used in the compositions of the present invention include, but are not limited to, Toray M40B 6000 50B (Toray Industries, Japan) and Graphil 34-700 12 K (Grafil Europe, Sutherland House, Matlock Road, Coventry, CV1 4JQ, UK).

The relative ratio by weight of fibres to powder is suitably in the range from 10E-04 to 1, preferably from 0.01 to 0.5.

The electrically conductive layer may be a film, an electrode or an electrically conductive track. There may be a preferred orientation of the electrically conductive fibres within the layer because this may enhance conductivity in a particular direction. For example, the ink may be used to form a track wherein the majority of the fibres are oriented along the direction of the track. It is possible that this will increase conductivity in the direction of the track.

The component fibres and powders may be mixed together using the following technique. An ink is made-up by hand, eg using the proportions 28.4wt% carbon powder, 17% Disperbyk 164 surfactant (Byk, Holland) and 54.6% pine oil, followed by triple-roll milling to ensure even mixing. This 'base' ink typically has a viscosity of approximately 100 Pa. The desired weight of fibre, pre-cut to the required length, is added to the base ink with manual stirring or for instance using a paddle-stirrer. After stirring for several minutes to ensure adequate mixing, the ink is ready for use. Such mixtures are suitably converted into films or tracks by applying the mixture to a substrate surface, preferably a smooth surface, by e.g. screen-printing or some similar technique and allowing the same to dry followed by suitable firing in an air or nitrogen atmosphere between 300-500°C.

The ink used in the present invention is particularly useful for making electrodes in optoelectronic devices such as solar cells (including photovoltaic cells). For instance in a solar cell, such electrodes are used for the purpose of transporting the electrical current generated by the photo-active components away to an external circuit or the next cell in a series or parallel configuration etc. The film may also serve to protect the internals of the cell from the external environment.

In a second aspect the present invention provides a solar cell comprising an electrically conductive layer formed by the use of an electrically conductive ink according to the present invention.

In a final aspect, the present invention provides a photovoltaic cell comprising an electrically conductive layer formed by the use of an electrically conductive ink according to the present invention.

The present invention is illustrated with reference to the following Example:

EXAMPLE 1

Carbon fibres, of length 1 mm were mixed in with a 'base' carbon powder ink made as described hereinbefore, by continuously stirring with a spatula for 5 minutes.

The weight ratio of carbon fibre to ink was 1:3. The fibre-containing ink was then used to form thin films of 1 x 5cm dimension on float glass substrates by screen-printing through a nylon mesh of 150 holes per inch. A single or double-pass print was normally sufficient to produce a coherent strip approximately 100 microns thick before drying.

- 5 After printing of the film, the piece was fired in an air oven at 450°C for 16 minutes in air.

The conductivity of the film was measured using a standard '4-point probe' technique using a Jandel scientific commercial instrument. This technique is widely
10 used in industry for measuring electrical conductivities. Test samples were prepared as 1 x 5cm strips on clear float glass substrates as described previously. Electrical contact was made either end of the longer side by coating silver-paint (Agar Scientific) overlays onto the samples with an overlap of 2mm each end. One current-driving and one potential-sensing lead were then connected to each end of the strip and the conductivity
15 read directly on a Hewlett Packard high-impedance systems meter. All tests were done at room temperature and humidity. The results of this test are shown in Table 1 below:

TABLE 1

Sample tested	Thickness of 1 x 5 cm strip (microns)	Resistance across length of strip (kilo-ohms)
Carbon particulate layer ink	30-40	25.8
As above but with added fibres	30-40	0.47

20

These results show that the combination of a carbon powder ink with carbon fibres results in a considerable reduction in the resistance of the resultant product.

CLAIMS

1. The use of an electrically conductive ink comprising an electrically conductive powder and electrically conductive fibres wherein the aspect ratio of the fibres is greater than 2:1, to form an electrically conductive layer.

2. The use of an electrically conductive ink as claimed in claim 1 wherein the electrically conductive powder comprises one or more of carbon, nickel, tungsten and F-doped tin oxide.

3. The use of an electrically conductive ink as claimed in claim 1 wherein the electrically conductive powder is carbon powder.

4. The use of an electrically conductive ink as claimed in any one preceding claims wherein the electrically conductive powder has a surface area in the range from 5 to 1000 m²/g.

5. The use of an electrically conductive ink as claimed any one of the preceding claims wherein the electrically conducting fibres are selected from carbon, nickel, tungsten and F-doped tin oxide.

6. The use of an electrically conductive ink as claimed in claim 5 wherein the electrically conducting fibres are carbon fibres.

7. The use of an electrically conductive ink as claimed in any one of the preceding claims wherein the electrically conductive fibres have a length of at least 1 micron.

8. The use of an electrically conductive ink as claimed in any one preceding claims wherein the electrically conductive fibres have a thickness of not more than 100 microns.

9. The use of an electrically conductive ink as claimed in any one of the preceding claims wherein the relative ratio by weight of electrically conductive fibres to electrically conductive powder is in the range from 10E-04 to 1.

10. A solar cell comprising an electrically conductive layer formed by the use of an electrically conductive ink as claimed in any one of the preceding claims.

11. A photovoltaic cell comprising an electrically conductive layer formed by the use
5 of an electrically conductive ink as claimed in any of claims 1-9.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 516 546 A (HARI SIEGFRIED ET AL) 14 May 1996 (1996-05-14)	1-9
Y	column 9, line 2 - line 38; claims 1-12	10, 11
X	US 5 877 110 A (TRUESDALE LARRY K ET AL) 2 March 1999 (1999-03-02) column 3, line 1 - line 3; column 4, line 20 - line 23; claims 1, 12, 24	1-6
X	WO 97 47699 A (CABOT CORP) 18 December 1997 (1997-12-18) claims 36, 40-43	1-6
A	EP 0 492 858 A (ICI PLC) 1 July 1992 (1992-07-01) example 11	1-6
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 98 34251 A (MAY BRONISLAV HENRY ;MONIOTTE PHILIPPE GERARD (BE); COLEMAN JAMES) 6 August 1998 (1998-08-06) page 13, line 24 - line 27 ---	10,11
A	US 5 942 048 A (ICHINOSE HIROFUMI ET AL) 24 August 1999 (1999-08-24) column 15, line 1 - line 8; claims 1,3; examples 2-1,2-6 ---	10,11
A	DATABASE WPI Section Ch, Week 198750 Derwent Publications Ltd., London, GB; Class A82, AN 1987-353252 XP002179923 & JP 62 257976 A (SEIKO EPSON CORP), 10 November 1987 (1987-11-10) abstract -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 01/02912

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5516546	A	14-05-1996	DE 4317302 A1	01-12-1994
			CA 2124133 A1	26-11-1994
			EP 0626430 A1	30-11-1994
			FI 942402 A	26-11-1994
			SG 49822 A1	15-06-1998
<hr/>				
US 5877110	A	02-03-1999	US 5707916 A	13-01-1998
			US 4663230 A	05-05-1987
			AT 192514 T	15-05-2000
			AU 661705 B2	03-08-1995
			AU 2217792 A	28-01-1993
			AU 3182189 A	25-08-1989
			AU 689654 B2	02-04-1998
			AU 3663995 A	15-02-1996
			BR 8905294 A	21-08-1990
			CA 1338304 A1	07-05-1996
			CA 2005642 A1	16-06-1990
			DE 68929201 D1	08-06-2000
			DE 68929201 T2	02-11-2000
			DK 477089 A	27-09-1989
			EP 0353296 A1	07-02-1990
			EP 0619388 A1	12-10-1994
			EP 0969128 A2	05-01-2000
			FI 894585 A	27-09-1989
			IL 89092 A	24-06-1994
			IL 109062 A	31-10-1996
			JP 10121334 A	12-05-1998
			JP 3024697 B2	21-03-2000
			JP 10121335 A	12-05-1998
			JP 2503334 T	11-10-1990
			JP 2982819 B2	29-11-1999
			KR 9615658 B1	20-11-1996
			NO 304660 B1	25-01-1999
			WO 8907163 A1	10-08-1989
			US 5611964 A	18-03-1997
			US 5500200 A	19-03-1996
			ZA 8900679 A	29-11-1989
			AT 141862 T	15-09-1996
			AU 637429 B2	27-05-1993
			AU 6666090 A	24-01-1991
			AU 600505 B2	16-08-1990
			AU 7703287 A	11-01-1988
			CA 1321863 A1	07-09-1993
			DE 3751885 D1	02-10-1996
			DE 270666 T1	24-11-1988
			DK 54288 A	03-02-1988
			EP 0270666 A1	15-06-1988
			FI 880546 A	05-02-1988
			IL 82787 A	21-06-1992
			JP 2862227 B2	03-03-1999
			JP 8199431 A	06-08-1996
			JP 2860276 B2	24-02-1999
			JP 82462 A	
<hr/>				
WO 9747699	A	18-12-1997	US 5707432 A	13-01-1998
			US 5803959 A	08-09-1998
			AU 3307897 A	07-01-1998
			AU 726728 B2	16-11-2000

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 01/02912

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9747699	A		AU 3308697 A	07-01-1998
			CA 2258188 A1	18-12-1997
			CN 1227584 A	01-09-1999
			DE 69706298 D1	27-09-2001
			EP 0904327 A1	31-03-1999
			EP 0910611 A1	28-04-1999
			JP 2000512670 T	26-09-2000
			JP 2000512329 T	19-09-2000
			WO 9747699 A1	18-12-1997
			WO 9747692 A1	18-12-1997
			US 5922118 A	13-07-1999
			US 5885335 A	23-03-1999
EP 0492858	A	01-07-1992	AU 658848 B2	04-05-1995
			AU 8968391 A	25-06-1992
			CA 2058104 A1	22-06-1992
			EP 0492858 A2	01-07-1992
			JP 5182512 A	23-07-1993
			NZ 240924 A	26-08-1993
			PT 99897 A	29-01-1993
			ZA 9109811 A	28-10-1992
WO 9834251	A	06-08-1998	AU 6139298 A	25-08-1998
			WO 9834251 A1	06-08-1998
US 5942048	A	24-08-1999	JP 7321351 A	08-12-1995
			JP 2750085 B2	13-05-1998
			JP 7335921 A	22-12-1995
			JP 7321353 A	08-12-1995
			JP 8046226 A	16-02-1996
			JP 8046230 A	16-02-1996
			AU 695669 B2	20-08-1998
			AU 2013495 A	30-11-1995
			CN 1150338 A	21-05-1997
			EP 0684652 A2	29-11-1995
			KR 195685 B1	15-06-1999
JP 62257976	A	10-11-1987	NONE	

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